PB-227 644

BATCH ADSORPTION KINETICS WITH CHEMICAL REACTION

Jeffrey S. Hsieh, et al

Syracuse University
Syracuse, New York

November 1969

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE
5285 Port Royal Road, Springfield Va. 22151

PB 227 644

Research Report 69-2

BATCH ADSORPTION KINETICS WITH CHEMICAL REACTION

by

Jeffrey S. Hsieh

Raffi M. Turian

and

Chi Tien, Principal Investigator

Submitted to:

Federal Water Pollution Control Administration

Under Grant No. 17020 DZO

Department of Chemical Engineering and Metallurgy

Syracuse University

Syracuse, New York

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

ABSTRACT

Theoretical solutions for adsorption from a liquid solution onto solid iso-dimensional spherical adsorbent particles were obtained. The purpose of the work was to obtain a description of the adsorption process involving waste water-granular activated carbon, which, together with experimental data on batch adsorption kinetics, would permit evaluation of diffusion coefficients for the system. A nonlinear, Freundlich type, adsorption isotherm, and chemical reaction in the liquid phase governed by a modified first order rate equation were used. The adsorption isotherm used has the form

$$q_E = AC_E^a$$

and the rate of chemical reaction is given by

$$R = -k(C - C_{B_E}) \quad \text{for } C > C_{B_E}$$

$$= 0 \qquad \text{for } C \leq C_{B_E}$$

These equations were chosen because, from experiments, they were found suitable for the waste water-activated carbon system.

Because of the nonlinear nature of the equations, numerical solutions for the solute concentration histories in the bulk solution were generated for two rate-controlling mechanisms: internal diffusion and pore diffusion. These concentration histories were generated for various values of the pertinent parameters governing the process. The details of the theoretical development are described in this report, and the computer programs developed for the numerical calculations are given in the Appendix.

TABLE OF CONTENTS

	Page
LIST OF FIGURES	ii
LIST OF TABLES	iii
I. INTRODUCTION	1
II. FORMULATION OF THE PROBLEM	4
A. Internal Diffusion Model	4
B. Pore Diffusion Model	8
III. NUMERICAL RESULTS	12
A. Internal Diffusion Model	12
B. Pore Diffusion Model	23
LITERATURE CITED	29
NOMENCLATURE	30
APPENDIX I - Computer Program for Calculation of Concentration Histories for Internal Diffusion Model	32
APPENDIX II - Computer Program for Calculation of Concentration Histories for Pore Diffusion Model	35

LIST OF FIGURES

Figure 1	Theoretical Concentration History for Internal Diffusion - No Chemical Reaction
Figure 2	Theoretical Concentration History for Internal Diffusion with Chemical Reaction
Figure 3	Effect of Time Increment Size on Computed Concentration History
Figure 4	Effect of Value of $\Delta\theta$ for Different Initial Concentrations
Figure 5	x^2-Plot for Internal Diffusion Computations
Figure 6	Effect of Decay of Waste Water on Computed Adsorption Kinetics
Figure 7	Effect of Freundlich Exponent on Concentration History
Figure 8	Concentration History for Pore Diffusion Model
Figure 9	Effect of Time Increment Size on Computed Concentration History for Pore Diffusion
Figure 10	x^2-Plot for Internal Diffusion Computations

LIST OF TABLES

Table 1(a)	Theoretical Concentration History for Internal Diffusion-No Chemical Reaction
Table 1(b)	Theoretical Concentration History for Internal Diffusion with Chemical Reaction
Table 2	Theoretical Concentration History for Pore Diffusion

I. INTRODUCTION

The investigation described in this report is an outgrowth of an experimental study of batch adsorption kinetics relating to the removal of organic contaminants from waste water using granular activated carbon. The characterization of the adsorption process involving the waste water-activated carbon system is necessary for design of carbon columns for waste water treatment, and the experimental study was instituted for this purpose.

In order to interpret the batch adsorption data properly, theoretical relationships for the concentration history under the same conditions which prevailed in the experiments were needed. Although the literature abounds with such theoretical solutions, their use in the case under consideration is precluded inasmuch as they do not take into account certain important features characteristic of the waste water-activated carbon adsorption system. The dissolved organic matter in waste water is generally composed of a variety of materials which cannot all be identified individually, and, at any rate, these vary from one waste water to another. For convenience, the organic contaminant content is expressed in terms of its equivalent total organic carbon (TOC). With contaminant concentrations expressed in terms of TOC, the adsorption isotherm for the waste water-granular activated carbon system was found to be (1)

$$q_E = 1.65 \times 10^{16} C_E^{3.68} \qquad \text{(I-1)}$$

at 30°C. In equation (I-1) q_E is the gram of TOC adsorbed per gram activated carbon, and C_E is the gram of TOC per cc waste water. The nonlinear nature of the adsorption isotherm, depicted by equation (I-1), means that the governing equations describing the batch adsorption process are nonlinear. The mathematical analysis of the problem is therefore complicated.

An additional complicating factor arises from the decay of organic contaminants (with attendant decrease in the TOC) resulting from bacterial action. The long duration of the batch adsorption experiments (up to 14 days) necessitates the incorporation of this effect in the analysis, thereby insuring correct interpretation of the experimental results, even though the effect may not be important in fixed-bed carbon column design. The empirical rate equation for the waste water decay data is

$$R = -k(C - C_{B_E}) \quad \text{for } C \geq C_{B_E} \tag{I-2}$$

where C is the TOC concentration, and C_{B_E} is the asymptotic value of the TOC for large time, i.e. when no further decrease in C occurs. The concentration C_{B_E} refers to the part of the organic contaminant content which is biologically resistant.

It is obvious, therefore, from the foregoing discussion, that theoretical solutions of batch adsorption processes characterized by a nonlinear Freundlich type of adsorption isotherm (Eq. I-1), and a chemical reaction of the type depicted in equation (I-2) are required for proper evaluation of the adsorption parameters. This task, in essence, constitutes the main object of the present work.

A large body of solutions relating to adsorption processes characterized by linear adsorption isotherms exists. Most of the classical examples of this type of work are presented in Crank's (2) book. Adsorption kinetics for systems with Langmuir type of equilibrium relationship have also been studied by several investigators including the recent work by Weber and his co-workers (3,4). None of these studies includes consideration of chemical reaction.

For systems exhibiting nonlinear adsorption isotherms, the mathemathematical problem resists analytical solution. Consequently, numerical

methods must be used. A numerical technique for the solution of batch adsorption in systems possessing nonlinear adsorption isotherms was developed by Tien (5,6). The presence of chemical reaction in the liquid phase was not considered, however.

In the present work we consider the specific case of batch adsorption with chemical reaction in the liquid phase. The main assumptions made are that the system possesses a Freundlich adsorption isotherm, and that, because of vigorous mixing, the liquid phase resistance to mass transfer is negligible. Two cases, based on the assumed rate-controlling mechanism, are considered: internal diffusion and pore diffusion. For the internal diffusion model the method of solution represents an extension and refinement of the method used in earlier work (6). For the pore diffusion model, Crank-Nicholson schemes were used to solve the diffusion problem. These calculations are described in detail below.

II. FORMULATION OF THE PROBLEM

A. Internal Diffusion Model

We consider a batch adsorption process in which a fixed quantity of liquid solution with initial concentration C_o is brought into contact with a fixed amount of adsorbent under isothermal conditions. The adsorbent particles are assumed to be spherical and of uniform size. The adsorption isotherm for the system is of the Freundlich type, i.e.

$$q^* = A \cdot C^{*a} \tag{II-1}$$

The mixing of the liquid is assumed vigorous enough to permit neglecting the liquid phase resistance so that the solution adhering to the adsorbent surface has the same concentration as that in the bulk of the liquid phase. In the liquid phase chemical reaction takes place at a rate represented by

$$R = - k(C - C_{B_E}) \quad C > C_{B_E} \tag{II-2}$$

in which C_{B_E} is a constant.

An overall material balance for the system is

$$V \frac{dC}{dt} + M \frac{dq}{dt} - VR = 0 \tag{II-3}$$

in which

V = volume of the liquid solution

C = concentration in the liquid (mass/unit volume)

M = mass of adsorbent

q = average concentration in the adsorbent (mass/unit mass)

In the internal diffusion model the adsorbent is assumed to be a homogeneous solid, and the mass transfer of solute within the adsorbent is described by Fick's law of diffusion. Accordingly, the concentration

distribution within the particle, $q_i(r,t)$, is obtained from a solution of the diffusion equation together with appropriate boundary conditions, and the average concentration within a single particle, q, is obtained by integration over the particle volume. Thus,

$$q = \frac{3}{b^3} \int_o^b q_i(r,t)\, r^2 dr \qquad \text{(II-4)}$$

in which b is the radius of the particle. The concentration distribution q_i is the solution of the equation

$$\nabla^2 q_i = \frac{1}{D} \frac{\partial q_i}{\partial t} \quad 0 \leq r \leq b,\ t > 0 \qquad \text{(II-5)}$$

Subject to the initial and boundary conditions

$$q_i = 0 \quad \text{for } t \leq 0,\ 0 \leq r \leq b \qquad \text{(II-6a)}$$

$$q_i = q_s \quad \text{for } r = b,\ t > 0 \qquad \text{(II-6b)}$$

Aside from Equation (II-1), the relationship between the concentrations in the two phases can also be deduced on the basis of the assumptions that equilibrium conditions prevail at solid-liquid interfaces, and that the Freundlich type of adsorption isotherm is followed. Since, as previously stated, liquid phase resistance is neglected, the liquid concentration at the particle surface is the same as that in the bulk solution, and q_s and C are related by

$$q_s = AC^a \qquad \text{(II-7)}$$

Following the procedure developed by Tien (5), and converting to dimensionless variables, we reduce Equation (II-2) through Equation (II-7) to

$$\frac{\partial \alpha}{\partial \theta} + \frac{\partial \beta}{\partial \theta} + \delta \cdot \Phi = 0 \qquad \text{(II-8)}$$

$$\frac{\partial \beta}{\partial \theta} = \frac{3}{2\pi} \int_0^\theta \frac{\partial \beta_s}{\partial \lambda} \left[\frac{1}{\sqrt{\theta - \lambda}} - \frac{1}{2} \right] d\lambda \qquad \text{(II-9)*}$$

$$\Phi = \begin{cases} \alpha - \alpha_{B_E} & \text{for } \alpha > \alpha_{B_E} \\ 0 & \text{for } \alpha \leq \alpha_{B_E} \end{cases} \qquad \text{(II-10)}$$

$$\beta_s = \alpha^a \qquad \text{(II-11)}$$

The initial conditions are:

$$\theta \leq 0: \quad \alpha = \alpha_o, \ \beta = 0 \qquad \text{(II-12)}$$

The dimensionless quantities in these equations are defined by the relations

$$\alpha = \left(\frac{MA}{V}\right)^{1/(a-1)} C \qquad \text{(II-13a)}$$

$$\beta = \left(\frac{M}{V}\right)\left(\frac{MA}{V}\right)^{1/(a-1)} q \qquad \text{(II-13b)}$$

$$\theta = \frac{4\pi D}{b^2} t \qquad \text{(II-13c)}$$

$$\delta = \frac{Kb^2}{4\pi D} \qquad \text{(II-13d)}$$

Equations (II-8) through (II-13) represent, with due reference to the conditions stated above, the complete description of the batch adsorption process using the internal diffusion model. The pertinent physical parameters for the system are:

1. Initial concentration parameter, $\alpha_o = \left(\frac{MA}{V}\right)^{1/(a-1)} C_o$
2. Chemical reaction parameter, $\delta = (kb^2/4\pi D)$.
3. Exponent in the adsorption isotherm equation, a.

---

*The derivation of Eq. (II-9) is given by Tien (5).

The system of Equations (II-8) through (II-12) cannot be solved analytically except in the linear case obtained when a = 1. For a ≠ 1 numerical techniques must be used. The numerical procedure employed is described next.

Equation (II-8) is rewritten in the form

$$\left.\frac{\partial\beta}{\partial\theta}\right|_j = -\left.\frac{\partial\alpha}{\partial\theta}\right|_j - \delta(\alpha_j - \alpha_{B_E})$$

$$\simeq -\frac{\alpha_j - \alpha_{j-1}}{\Delta\theta} - \delta(\alpha_j - \alpha_{B_E}) \qquad \text{(II-14)}$$

The subscript j refers to the value corresponding to the jth increment of θ (i.e. θ = jΔθ). The backward difference approximation is used to express ∂α/∂θ. Equation (II-9) can be written as

$$\left.\frac{\partial\beta}{\partial\theta}\right|_j = \frac{3}{2\pi}\sum_{k=0}^{j-1}\int_{k\Delta\theta}^{(k+1)\Delta\theta}\frac{\partial\beta_s}{\partial\lambda}\left[\frac{1}{\sqrt{\theta-\lambda}} - \frac{1}{2}\right]d\lambda$$

$$\simeq \frac{3}{2\pi}\left(\frac{1}{\Delta\theta}\right)\left\{\alpha_j^a\, 2\sqrt{\Delta\theta} - \alpha_j^a\frac{\Delta\theta}{2} - 2\sqrt{\Delta\theta}\sum_{k=1}^{j-1}\alpha_k^a K_{j-k}\right\} \qquad \text{(II-15)}$$

where

$$K_{j-k} = 2\sqrt{j-k} - \sqrt{j-(k-1)} - \sqrt{j-(k+1)} \qquad \text{(II-16)}$$

Details of the procedure used to obtain the expression given by Equation (II-15) can be found elsewhere (5,6). Combining Equations (II-14), (II-15), and (II-16), and rearranging slightly, we get

$$B\alpha_j^a + \alpha_j + F+G\,(\alpha_j - \alpha_{B_E}) = 0 \qquad \text{(II-17)}$$

$$\alpha = \alpha_o \quad \text{at } \theta = 0$$

with

$$B = \frac{3}{\pi}\sqrt{\Delta\theta} - \frac{3}{4\pi}\Delta\theta \qquad \text{(II-18a)}$$

$$F = -\alpha_{j-1} - \frac{3}{\pi}\sqrt{\Delta\theta}\sum_{k=1}^{j-1} K_{j-k}\alpha_k^a \qquad \text{(II-18b)}$$

$$G = \delta\cdot\Delta\theta \qquad \text{(II-18c)}$$

The term $G(\alpha_j - \alpha_{B_E})$ is omitted when $\alpha_j \leq \alpha_{B_E}$ as stated before.

Equations (II-17) and (II-18) provide the basis for calculation of the concentration history, i.e. α vs. θ, for specified values of the parameters α_o, δ and a.

B. Pore Diffusion Model

The problem considered in this section is the same as the one discussed in Section II-A in every respect except in relation to the model considered for the adsorption process. Here, the rate of adsorption is assumed to be controlled by the diffusion of solutes through the liquid filling the pores of the adsorbent. Accordingly, the solid and liquid phase concentrations are assumed to be in equilibrium at every point within the adsorbent. In addition, as before, the agitation is supposed vigorous enough to preclude entirely the need to consider liquid phase resistance.

An overall material balance is

$$V(C_o - C_b) + V\int_o^t R\cdot dt = (M)\cdot(q) \qquad \text{(II-19)}$$

where C_b denotes the concentration in the bulk of the liquid phase. The average concentration of adsorbate on the adsorbent, for the pore diffusion model, is given by

$$q = \frac{3}{b^3\rho}\int_o^b (\varepsilon C + \rho S)\, r^2 dr \qquad \text{(II-20)}$$

where

ε = the porosity of the adsorbent

C = the concentration of the liquid within the internal pore structure of the adsorbent

S = concentration at the surface of the adsorbent matrix

ρ = bulk density of the adsorbent

b = radius of the adsorbent particle

The diffusion equation for the pore diffusion model is

$$\varepsilon \left(\frac{\partial C}{\partial t} - R\right) + \rho \frac{ds}{dt} = D_p \frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) \qquad \text{(II-21)}$$

with the initial and boundary conditions

$$C = S = 0 \qquad 0 \leq r \leq b \qquad t \leq 0$$

$$C = C_b \qquad r = b \qquad t \geq 0$$

Based on the assumption that equilibrium prevails between the solid and liquid phase concentrations within the adsorbent, we have

$$S = A \cdot C^a \qquad \text{(II-22)}$$

Before proceeding with a solution of the system of Equations (II-19) through (II-22), we reduce them to non-dimensional form using the dimensionless quantities:

$$r^+ = r/b \qquad \text{(II-23a)}$$

$$t^+ = \frac{D_p}{\varepsilon b^2} t \qquad \text{(II-23b)}$$

$$C^+ = \left(A \frac{\rho}{\varepsilon}\right)^{\frac{1}{a-1}} C \qquad a \neq 1 \qquad \text{(II-23c)}^*$$

$$S^+ = \left[A \left(\frac{\rho}{\varepsilon}\right)^a\right]^{\frac{1}{a-1}} S \qquad \text{(II-23d)}^*$$

$$\phi_1 = \frac{3M}{\rho V} \varepsilon \qquad \text{(II-23e)} \qquad \phi_2 = \frac{\varepsilon b^2 k}{D_p} \qquad \text{(II-23f)}$$

*For a = 1, the definition above is not applicable. The solution for this particular case has been obtained by J.B. Rosen (J.Chem.Phys., 20, 387 (1952).

With these definitions, Equations (II-19) through (II-22) become

$$(C_o^+ - C_b^+) - \phi_2 \int_o^{t^+} (C_b^+ - C_{B_E}^+)dt^+ = \phi_1 \int_o^1 (C^+ + S^+)\, r^{+2}\, dr^+ \qquad \text{(II-24)}$$

$$\frac{\partial C^+}{\partial t^+} + \phi_2 (C^+ - C_{B_E}^+) + \frac{\partial S^+}{\partial t^+} = \frac{1}{r^{+2}} \frac{\partial}{\partial r^+} \left(r^{+2} \frac{\partial C^+}{\partial r^+}\right) \qquad \text{(II-25)}$$

$$S^+ = C^{+a} \qquad \text{(II-26)}$$

with

$$t^+ \leq 0,\ 0 \leq r^+ \leq 1,\ C^+ = S^+ = 0$$

If the Crank-Nicholson scheme is used for the approximation of derivatives by finite difference expressions, Equation (II-25) becomes

$$\frac{C_m^{i+1} - C_m^i}{(\delta t/2)} + \phi_2 \left[\frac{C_m^{i+1} + C_m^i}{2} - C_{B_E}\right] + \frac{S_m^{i+1} - S_m^i}{(\delta t/2)}$$

$$\simeq \frac{1}{m(\delta r_m)^2} \left[(m+1)(C_{m+1}^{i+1} + C_{m+1}^i) - 2m(C_m^{i+1} + C_m^i)\right.$$

$$\left. + (m-1)(C_{m-1}^{i+1} + C_{m-1}^i)\right] \qquad \text{(II-27)}$$

or

$$S_m^{i+1} = S_m^i + \frac{\delta t}{2m(\delta r_m)^2} \left[(m+1)(C_{m+1}^{i+1} + C_{m+1}^i) - 2m(C_m^{i+1} + C_m^i)\right.$$

$$\left. + (m-1)(C_{m-1}^{i+1} + C_{m-1}^i)\right] - (C_m^{i+1} - C_m^i) - \phi_2 \left(\frac{\delta t}{2}\right)\left(\frac{C_m^{i+1} + C_m^i}{2} - C_{B_E}\right) \qquad \text{(II-28)}$$

The superscript i and the subscript m refer to the time and space increments, respectively. The space increment δr_m is allowed to vary in size. The superscript "+" designating dimensionless quantities is omitted. The term containing ϕ_2 is dropped unless the quantity in brackets,

$\left[(C_m^{i+1} + C_m^i)/2 - C_{B_E} \right]$, is positive. The sphere is divided into N increments, and the above expressions apply for m=1 to m = N-1.

For m=0, i.e. at the center of the particle, the following expression is used:

$$S_o^{i+1} = S_o^i + (C_o^{i+1} - C_o^i) - \phi_2 \left[\frac{C_o^{i+1} + C_o^i}{2} - C_{B_E} \right] \delta t$$

$$+ \frac{3\delta t}{(\delta r)^2} \left[(C_1^{i+1} + C_1^i) - (C_o^{i+1} + C_o^i) \right] \qquad \text{(II-29)}$$

For m=N, i.e. at the particle surface, $C_N = C_b$ and Equation (II-24) should be used. If the two integrals in Equation (II-24) are calculated using Simpson's rule, the following expression is obtained:

$$C_N^i = C_b^i = C_o - \phi_2(\delta t) \left[\frac{(C_o - C_{B_E})}{2} + (C_N^1 - C_E) + (C_N^2 - C_{B_E}) \right.$$

$$\left. + \ldots . (C_N^{i-1} - C_{B_E}) + \frac{(C_N^i - C_{B_E})}{2} \right]$$

$$- \phi_1 \sum_{j=1}^{N} (j)^2 (C_j^i + S_j^i)(\delta r_j)^3 \qquad \text{(II-30)}$$

Again, the term in ϕ_2 is dropped unless all the terms in the square bracket are positive.

Equations (II-28), (II-29) and (II-30) provide the basis for the calculations. The relationship between S_i^m and C_i^m is provided by Equation (II-26).

III. NUMERICAL RESULTS

A. Internal Diffusion Model

The computation scheme in this case is based on Equation (II-17), i.e.

$$B\alpha_j^a + \alpha_j + F+G\,(\alpha_j - \alpha_{B_E}) = 0 \qquad \text{(II-17)}$$

$$\alpha_j = \alpha_o \quad \text{for } j = 0$$

The computation is straightforward, and involves essentially the solutions of a polynomial expression. This was done using Newton's iteration procedure and the physical condition that α is a monotomically decreasing function of θ.

The physical parameters for the internal diffusion model are α_o, a, and δ. Typical results for a few sets of values of the parameters were calculated and are shown in Table 1 as α/α_o vs θ. An alternate method of expressing the results is in terms of concentration difference ratio. If the contact time is infinite, the liquid and solid phases will be in equilibrium. For equilibrium concentrations C_∞ and q_∞ in the liquid and solid phases, respectively, a simple material balance gives

$$V\cdot C_\infty + Mq_\infty + Vk \int_o^t (C - C_{B_E})\, dt = V\cdot C_o \qquad \text{(III-1)}$$

or, in terms of the dimensionless variables defined before

$$\alpha_\infty + \alpha_\infty^a + \delta \int_o^\theta (\alpha - \alpha_{B_E})\, d\theta = \alpha_o \qquad \text{(III-2)}$$

But, from definition of α

$$\frac{C - C_\infty}{C_o - C_\infty} = \frac{\alpha - \alpha_\infty}{\alpha_o - \alpha_\infty} \qquad \text{(III-3)}$$

Thus, with α_∞ evaluated using Equation (II-17), the concentration difference ratio is determined according to Equation (III-3).

TABLE 1
(a) Theoretical Concentration History for
Internal Diffusion - No Chemical Reaction

$a = 4.0 \quad \delta = 0.0$

θ	α/α_o			
	$\alpha_o = 0.5$	$\alpha_o = 1.0$	$\alpha_o = 3.0$	$\alpha_o = 5.0$
0.005	0.99197	0.94672	0.66006	0.49643
0.010	0.98883	0.92907	0.61183	0.45167
0.015	0.98649	0.91689	0.58503	0.42817
0.020	0.98457	0.90743	0.56697	0.41287
0.025	0.98291	0.89964	0.55354	0.40175
0.030	0.98144	0.89299	0.54296	0.39312
0.035	0.98011	0.88719	0.53427	0.38613
0.040	0.97889	0.88203	0.52695	0.38028
0.045	0.97776	0.87739	0.52063	0.37527
0.050	0.97671	0.87317	0.51510	0.37091
0.055	0.97572	0.86929	0.51018	0.36705
0.060	0.97479	0.86571	0.50577	0.36361
0.065	0.97390	0.86239	0.50177	0.36050
0.070	0.97306	0.85928	0.49812	0.35767
0.075	0.97226	0.85637	0.49477	0.35508
0.080	0.97149	0.85363	0.49168	0.35269
0.085	0.97076	0.85103	0.48881	0.35048
0.090	0.97005	0.84858	0.48613	0.34843
0.095	0.96937	0.84625	0.48362	0.34650
0.100	0.96871	0.84403	0.48127	0.34470
0.105	0.96808	0.84191	0.47905	0.34301
0.110	0.96746	0.83988	0.47696	0.34141
0.115	0.96687	0.83794	0.47497	0.33990
0.120	0.96629	0.83608	0.47309	0.33847
0.125	0.96573	0.83429	0.47130	0.33711

TABLE 1
(b) Theoretical Concentration History for
Internal Diffusion with Chemical Reaction

$a = 4.0 \quad \delta = 100$

θ	α/α_o			
	$\alpha_o = 0.5$	$\alpha_o = 1.0$	$\alpha_o = 3.0$	$\alpha_o = 5.0$
0.005	0.86359	0.94672	0.66006	0.49643
0.010	0.77556	0.92907	0.61183	0.45167
0.015	0.71707	0.91689	0.58503	0.42817
0.020	0.67810	0.90743	0.56697	0.41287
0.025	0.65211	0.89964	0.55354	0.40175
0.030	0.63476	0.89299	0.54296	0.39312
0.035	0.62318	0.88719	0.53427	0.38613
0.040	0.61545	0.88203	0.52695	0.38028
0.045	0.61028	0.87739	0.52063	0.37527
0.050	0.60682	0.87317	0.51510	0.37091
0.055	0.60452	0.86929	0.51018	0.36705
0.060	0.60297	0.86571	0.50577	0.36361
0.065	0.60194	0.86239	0.50177	0.36050
0.070	0.60125	0.85928	0.49812	0.35767
0.075	0.60079	0.85637	0.49477	0.35508
0.080	0.60048	0.85363	0.49168	0.35269
0.085	0.60027	0.85103	0.48881	0.35048
0.090	0.60013	0.84858	0.48613	0.34843
0.095	0.60004	0.84625	0.48362	0.34650
0.100	0.59998	0.84403	0.48127	0.34470
0.105	0.59990	0.84191	0.47905	0.34301
0.110	0.59983	0.83988	0.47696	0.34141
0.115	0.59976	0.83794	0.47497	0.33990
0.120	0.59969	0.83608	0.47309	0.33847
0.125	0.59962	0.83429	0.47130	0.33711

The computations were carried out with an IBM 360/50 computer. The program was coded in FORTRAN language and is given in the Appendix. A few typical curves are shown in Figures 1 and 2. The effect of time increment size on the accuracy of the computations was studied empirically. Several examples are shown in Figures 3 and 4, which exhibit the computed concentration histories, resulting from seven different time increment sizes between 0.005 and 0.8, for the particular case $\alpha_o = 3.0$, $a = 4.0$ and $\delta = 100$. These results indicate that a $\Delta\theta \leq 0.01$ will be necessary for attainment of sufficient accuracy. However, for better accuracy, it may be necessary to employ two different time increment sizes using an x^2-plot. The extrapolation was found to give a higher value as shown in Figure 5.

The effect of chemical reaction in the liquid phase on the adsorption is shown in Figure 6. The particular cases demonstrated pertain to $\alpha_o = 0.5$, $a = 4.0$ and the two values for δ of 0 and 100. Clearly, the chemical reaction in the liquid phase has a marked effect on the concentration history. Indeed, the chemical decomposition makes such a large contribution to the sharp decline in concentration level that failure to take it into account would surely result in overestimated diffusion coefficients.

The effect of the magnitude of the exponent in the adsorption isotherm, i.e. a in Equation (II-1), is shown in Figure 7. For three different values of α_o, the concentration histories for $a = 4.0$ and $a = 6.0$ are depicted. For fixed α_o, the curves for the two a values turn out to be nearly parallel, which suggests that the diffusion coefficients, calculated by comparison of experimental data with the theoretical curves, are strongly sensitive to errors in the determination of the adsorption isotherm. Consequently, in view of the fact that the waste water-activated carbon adsorption data were found to exhibit considerable scatter (1), there is a

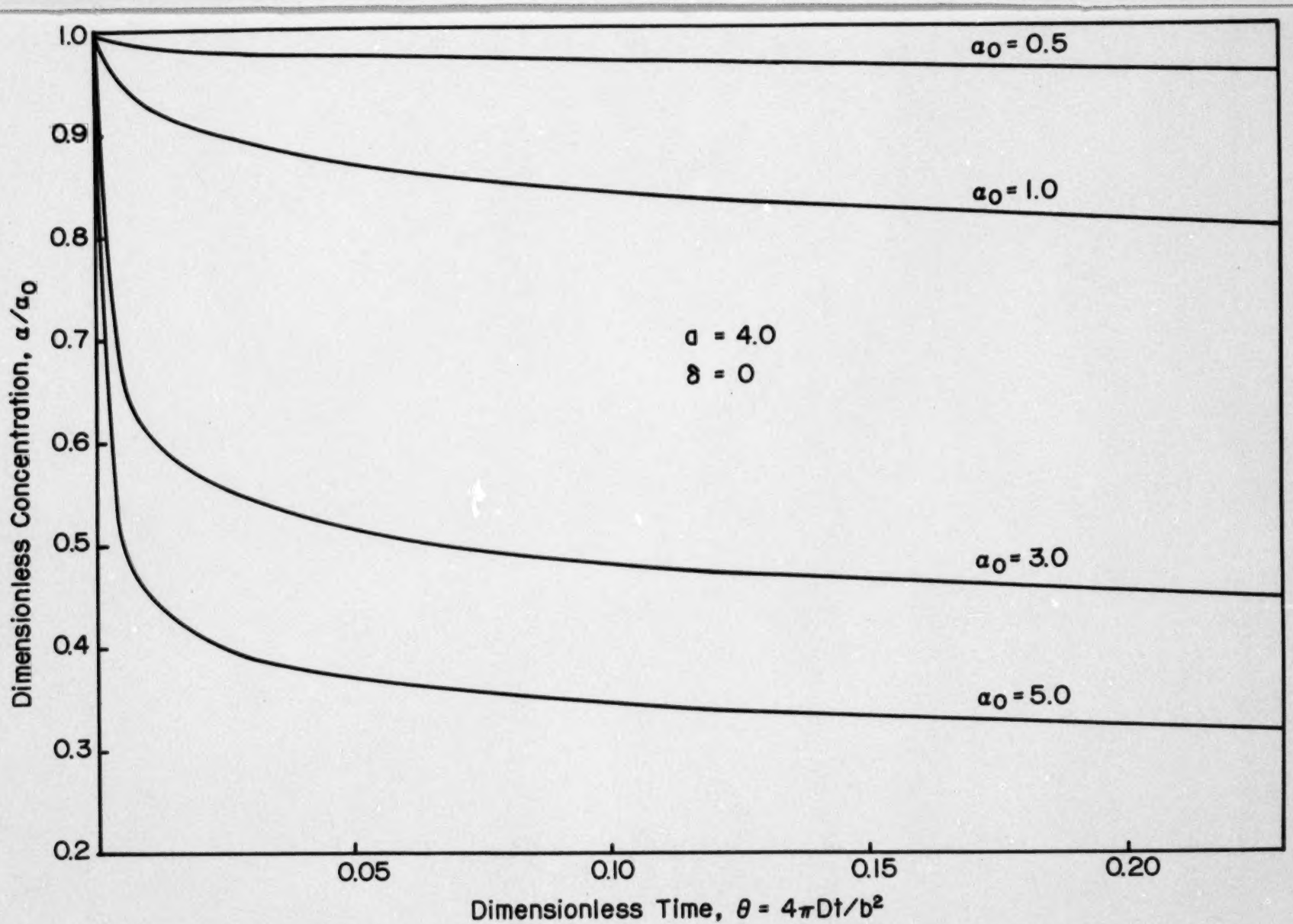

Fig. 1. Theoretical Concentration History for Internal Diffusion - No Chemical Reaction

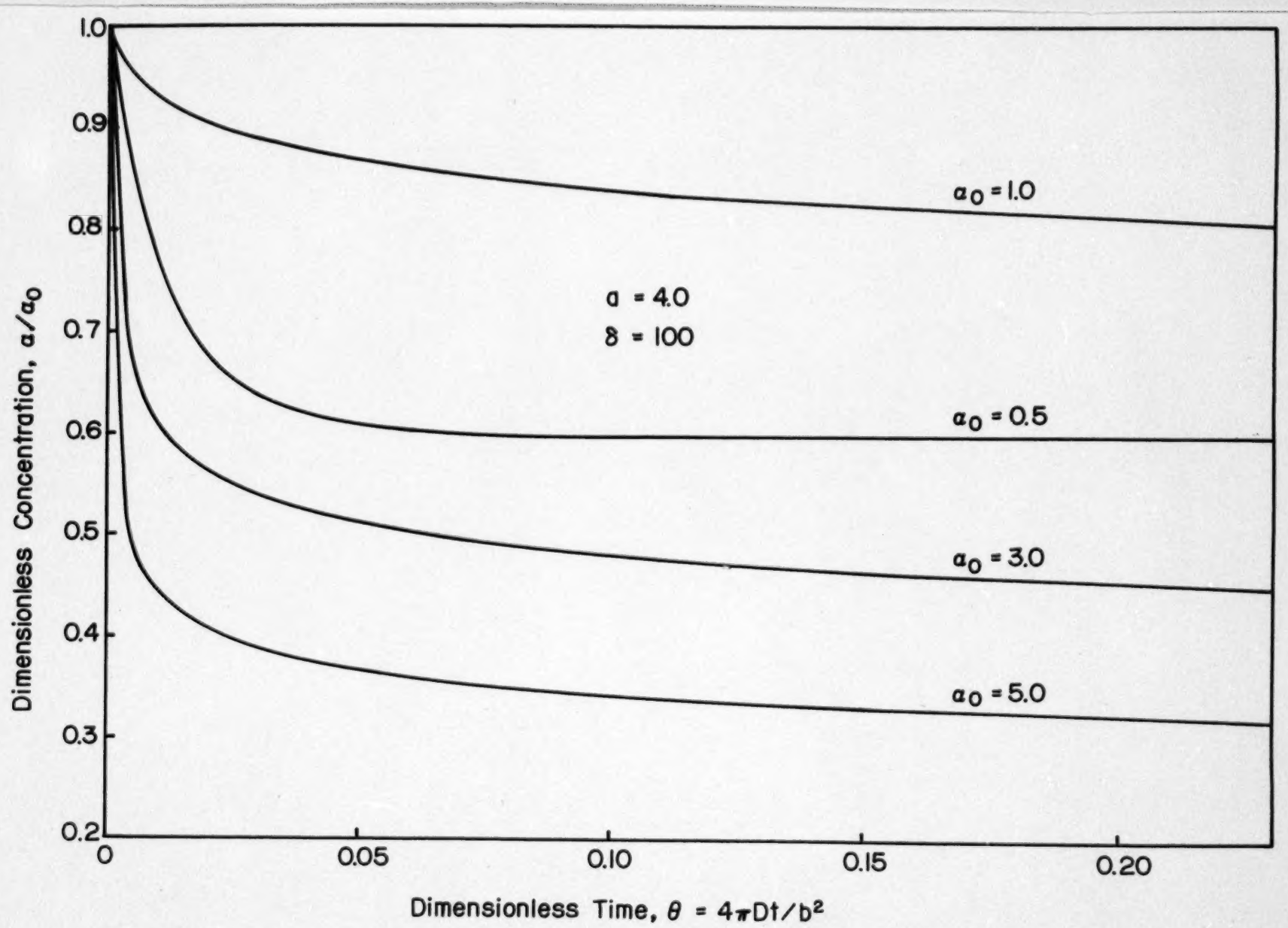

Fig. 2. Theoretical Concentration History for Internal Diffusion with Chemical Reaction

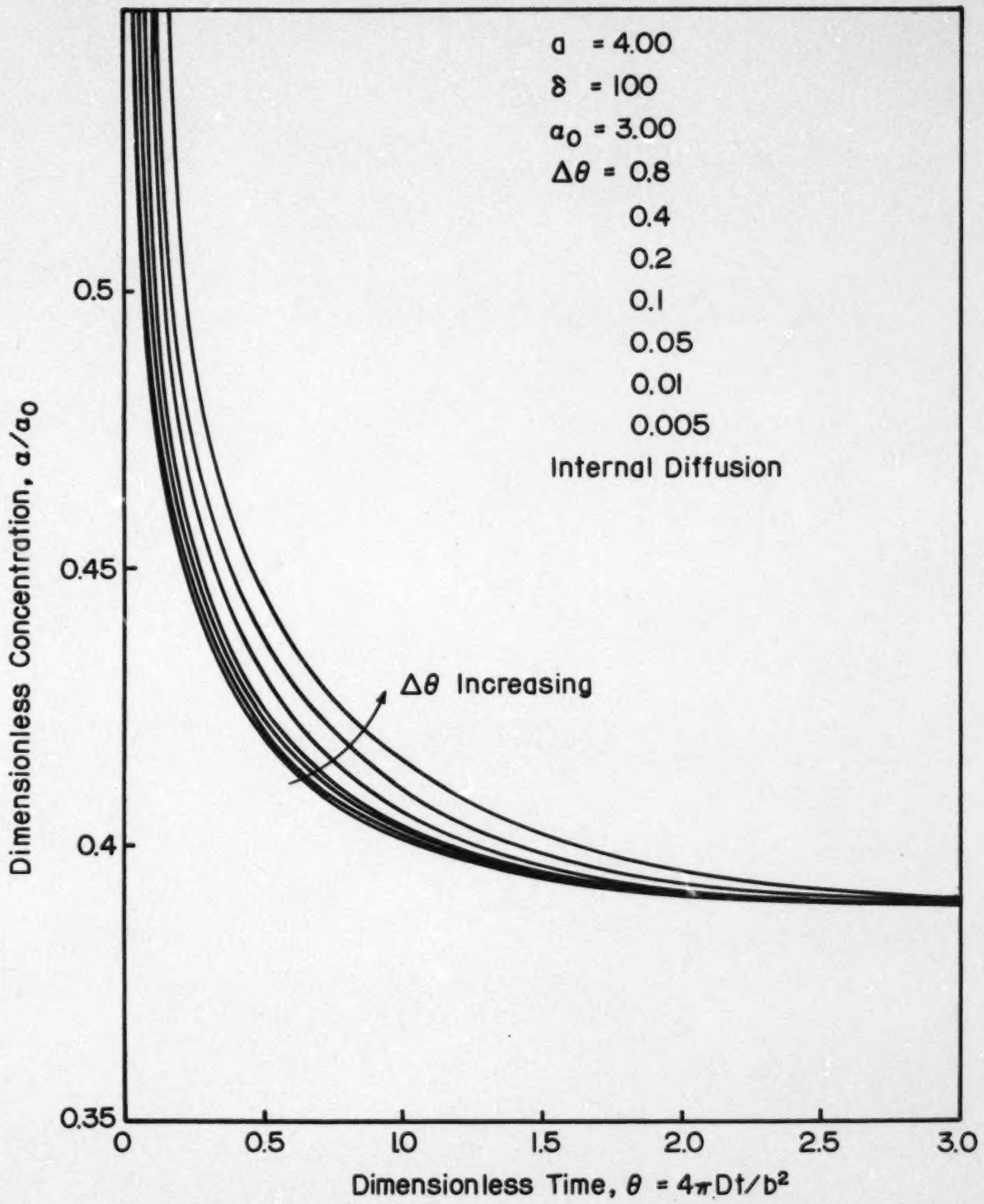

Fig. 3. Effect of Time Increment Size on Computed Concentration History

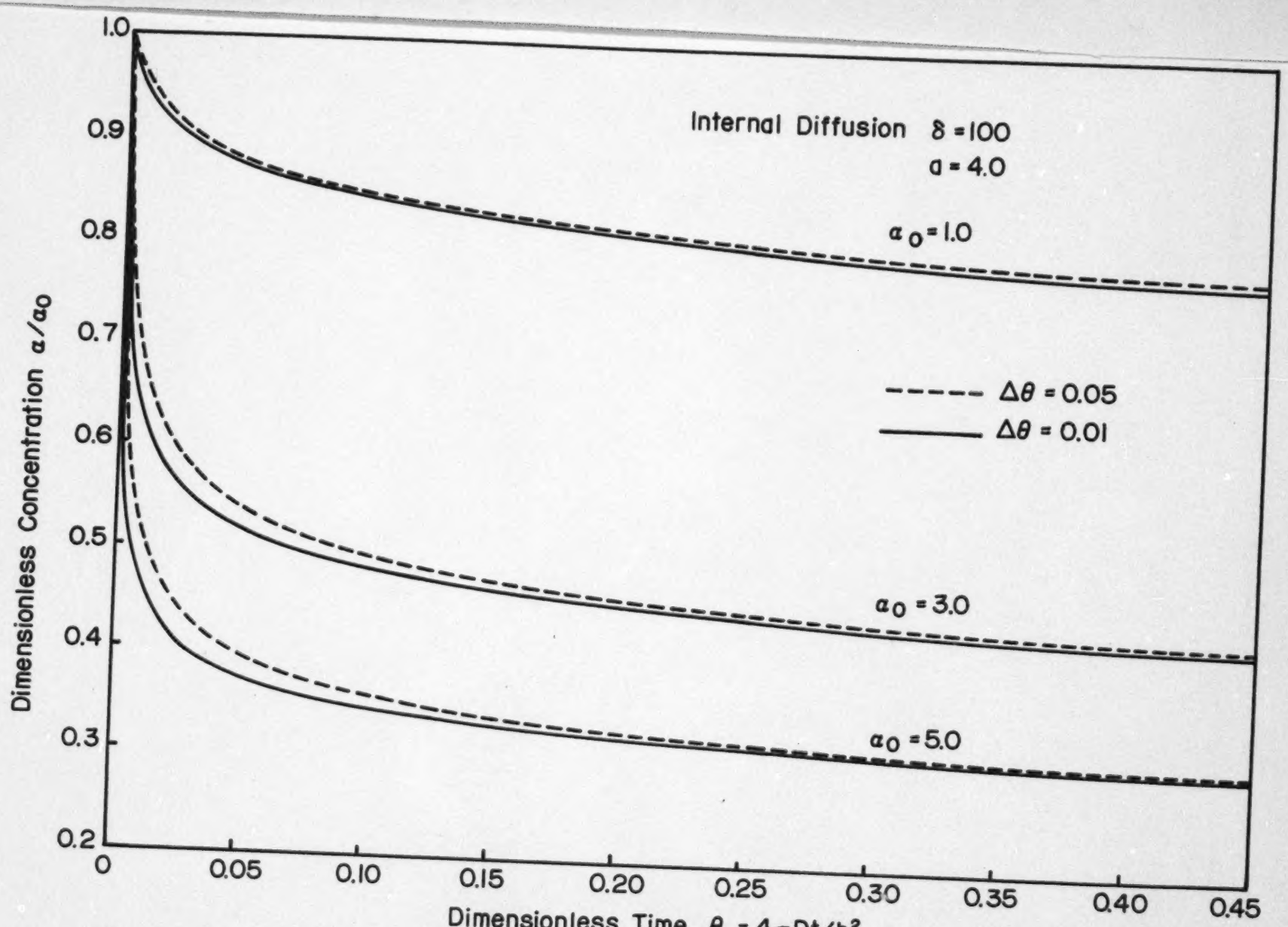

Fig. 4. Effect of Value of $\Delta\theta$ for Different Initial Concentrations

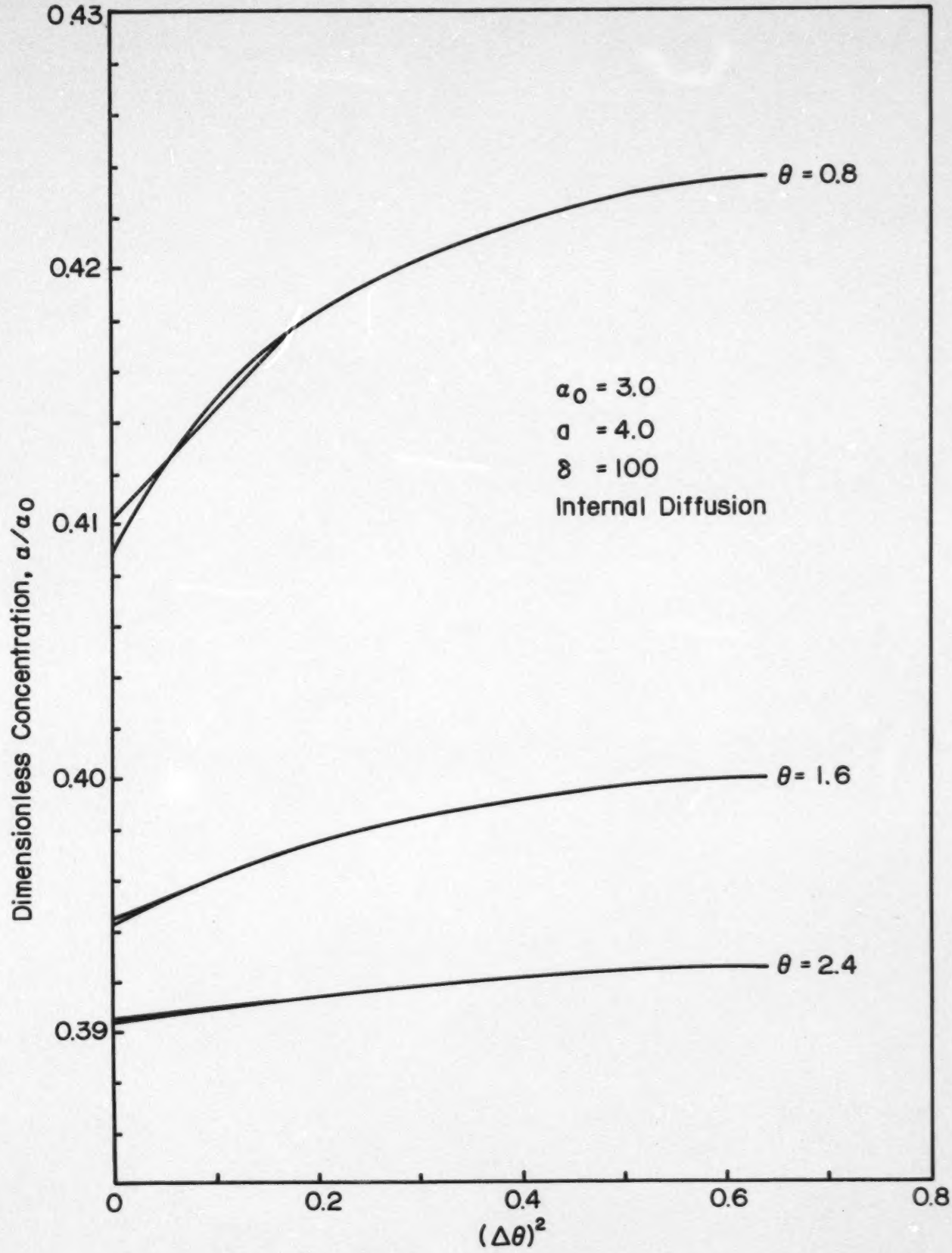

Fig. 5. x^2 - Plot for Internal Diffusion Computations

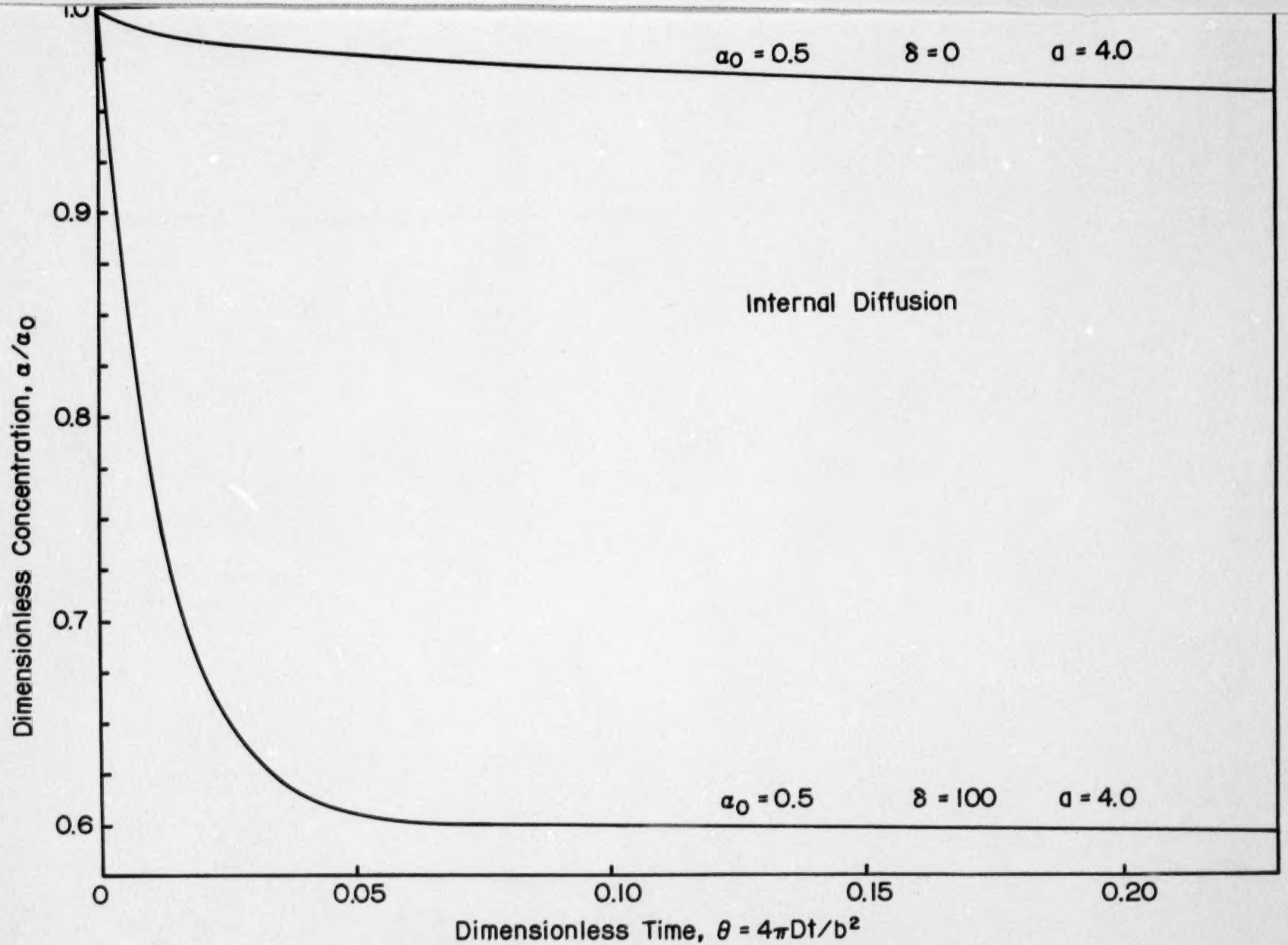

Fig. 6. Effect of Decay of Waste Water on Computed Adsorption Kinetics

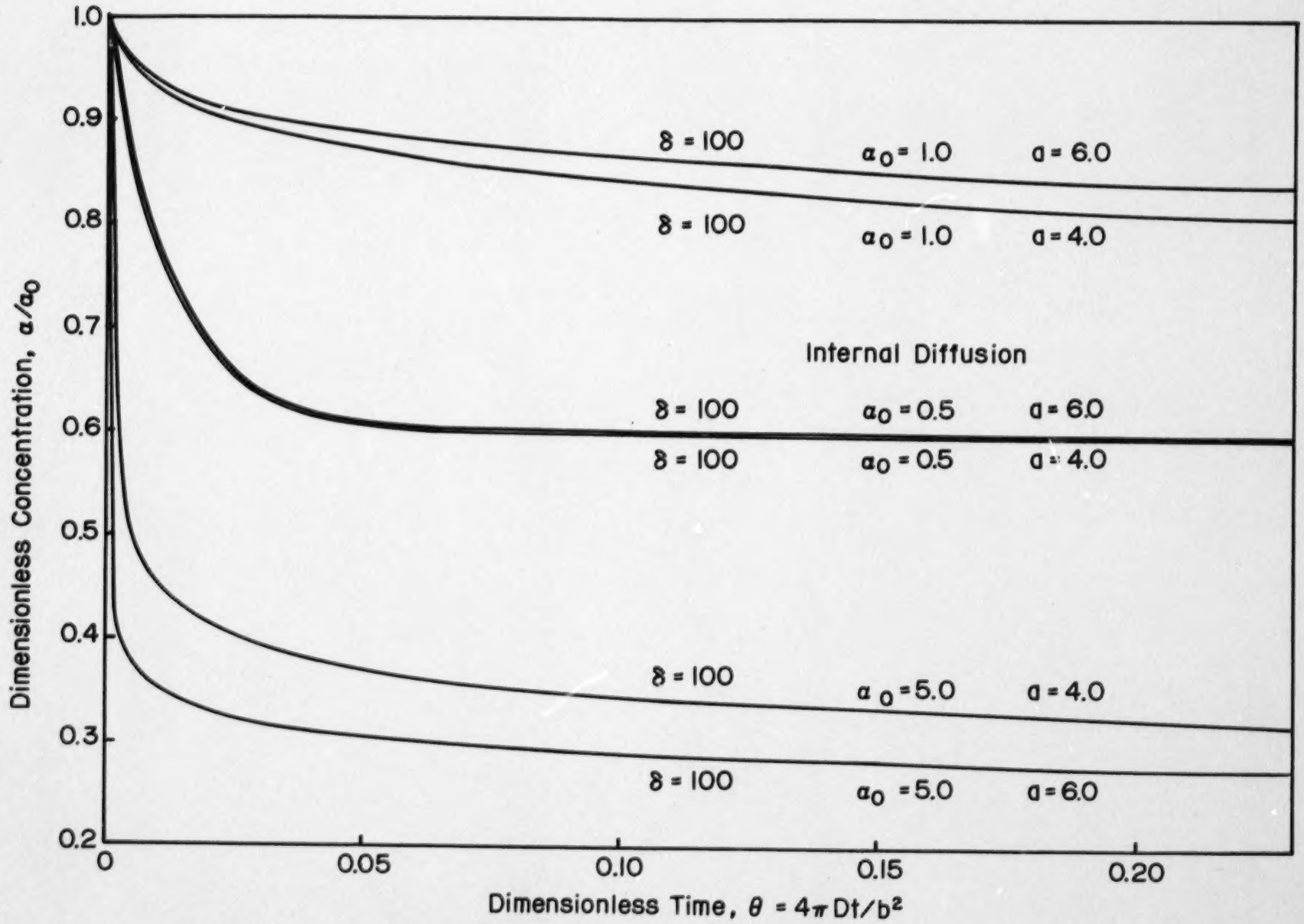

Fig. 7. Effect of Freundich Exponent on Concentration History

limit on the expected accuracy with which diffusion coefficients for this system can be determined.

B. Pore Diffusion Model

The computations in this case are more tedious because two independent variables are involved; r and also θ. The computation schemes are based on Equations (II-28), (II-29) and (II-30). Three equations are used in calculating the numerical values:

1. For $m = 0$

$$S_o^{i+1} = S_o^i - (C_o^{i+1} - C_o^i) - \phi_2 \left[\frac{C_o^{i+1} + C_o^i}{2} - C_{B_E} \right] \left(\frac{\delta t}{2}\right)$$

$$+ \frac{3\delta t}{(\delta r)^2} \left[(C_1^{i+1} + C_1^i) - (C_o^{i+1} + C_o^i) \right] \qquad \text{(II-29)}$$

2. For $0 < m < N$

$$S_m^{i+1} = S_m^i + \frac{\delta t}{2m(\delta r_m)^2} \left[(m+1)(C_{m+1}^{i+1} + C_{m+1}^i) - 2m(C_m^{i+1} + C_m^i) \right.$$

$$\left. + (m-1)(C_{m-1}^{i+1} + C_{m-1}^i) \right] - (C_m^{i+1} - C_m^i) - \phi_2 \left(\frac{\delta t}{2}\right) \left(\frac{C_m^{i+1} + C_m^i}{2} - C_{B_E} \right) \qquad \text{(II-28)}$$

3. For $m = N$

$$C_N^i = C_b^i = C_o - \phi_2(\delta t) \left[\frac{(C_o - C_{B_E})}{2} + (C_N^1 - C_{B_E}) + (C_N^2 - C_{B_E}) \right.$$

$$\left. + \ldots + (C_N^{i-1} - C_{B_E}) + \frac{C_N^i - C_{B_E}}{2} \right]$$

$$- \phi_1 \sum_{j=1}^{N} (j)^2 (C_j^i + S_j^i)(\delta r_j)^3 \qquad \text{(II-30)}$$

The computation program was coded in FORTRAN language and is given in the Appendix. The procedure is an iterative one because of the nature of the Crank-Nicholson formulation. The effects of chemical reaction in the liquid phase, and the magnitude of the adsorption isotherm exponent on the theoretical concentration history are similar to those discussed in relation to the internal diffusion model, and, therefore, need not be repeated. A few typical results are shown in Figure 8, with numerical data given in Table 2.

For the pore diffusion model, the spherical particle is subdivided into increments of unequal size. Starting with the smallest increment size at the sphere surface each succeeding increment is increased by adding the smallest increment size as we proceed toward the center of the sphere. Thus, $(\delta r)_{N-1} = 2(\delta r)_N$, $(\delta r)_{N-2} = 3(\delta r)_N$, $(\delta r)_{N-3} = 4(\delta r)_N$, and so on. By so doing, greater emphasis is placed on the initial uptake period of the adsorption process, since it is during this period that the experimental results can be obtained with the maximum accuracy. The effect of the time increment size used is shown in Figure 9. It is clear that provided a $\Delta\theta \leq 0.01$ is used no essential difference in the calculations can be observed. However, in the internal diffusion model the extrapolated value from the x^2-plot gives higher limiting values as shown in Figures 5 and 10.

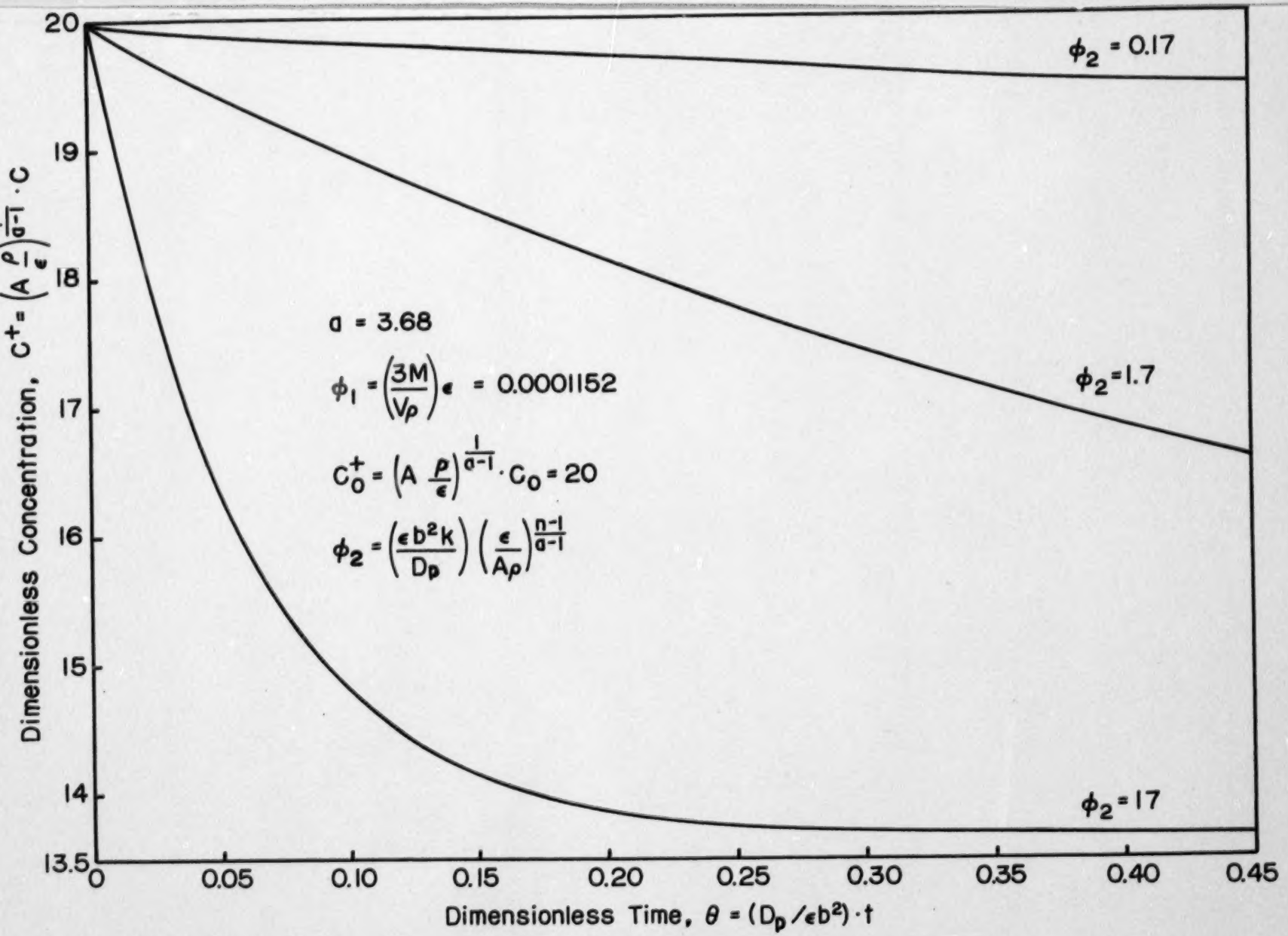

Fig. 8. Concentration History for Pore Diffusion Model

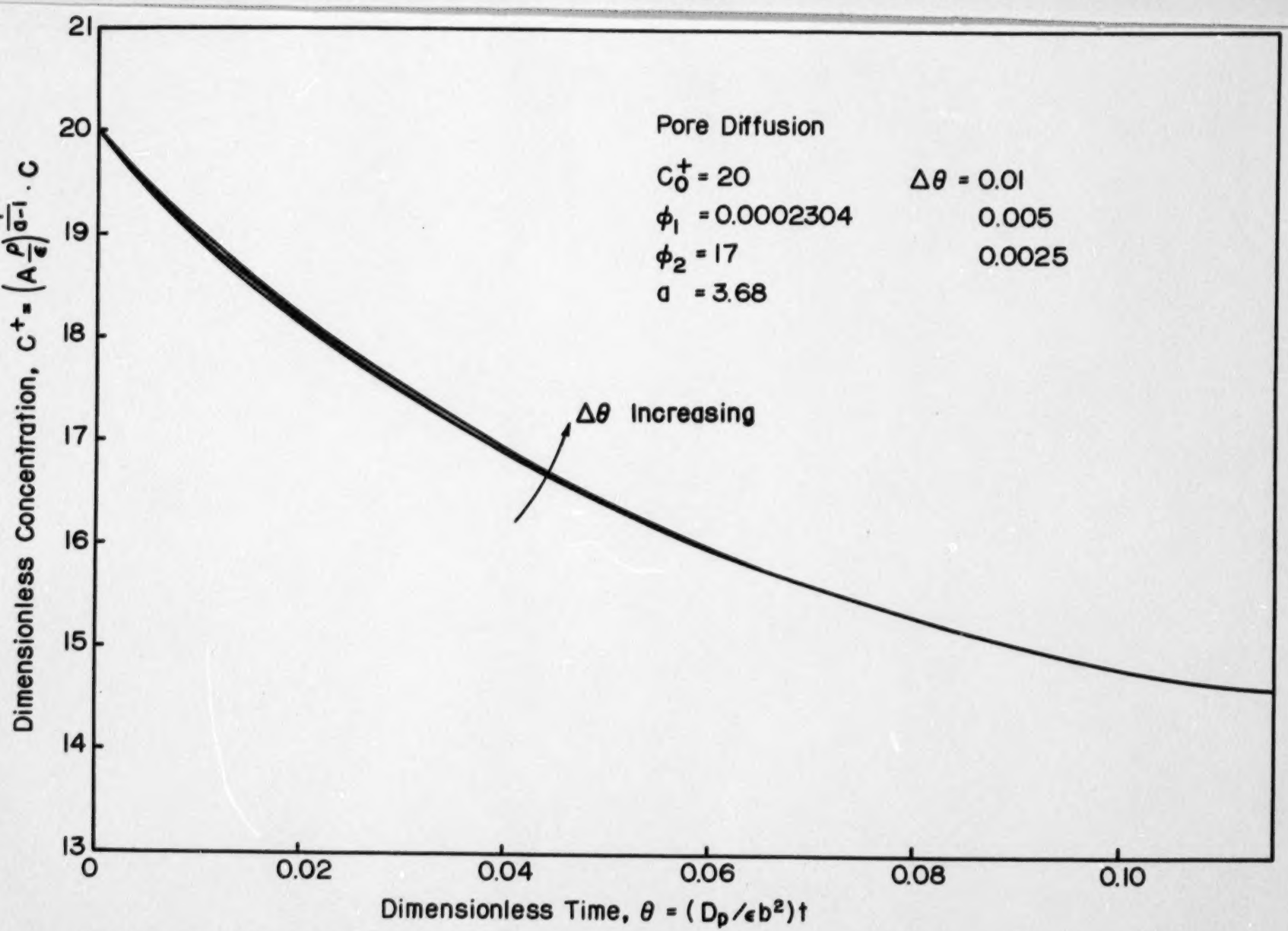

Fig. 9. Effect of Time Increment Size on Computed Concentration History for Pore Diffusion

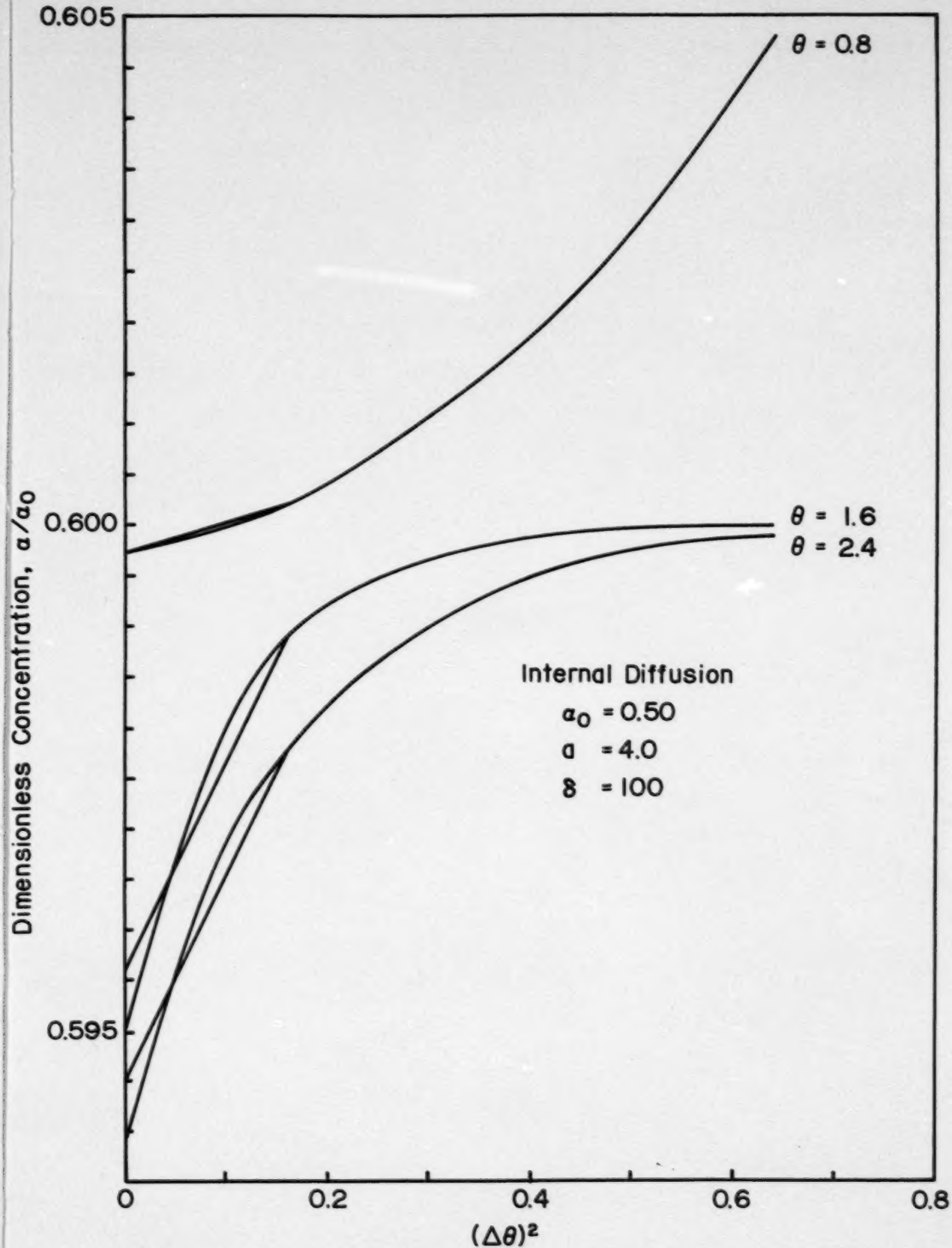

Fig. 10. x^2 - Plot for Internal Diffusion Computations

TABLE 2

Theoretical Concentration History for Pore Diffusion

$a = 3.68 \quad C_o^+ = 20 \quad \phi_1 = 1.152 \times 10^{-4} \quad \phi_2 = 17$

θ	C^+	θ	C^+
0.010	19.02767	0.130	14.37803
0.015	18.59256	0.135	14.32143
0.020	18.19244	0.140	14.26944
0.025	17.82493	0.145	14.22169
0.030	17.48736	0.150	14.17784
0.035	17.17730	0.155	14.13756
0.040	16.89250	0.160	14.10056
0.045	16.63092	0.165	14.06658
0.050	16.39066	0.170	14.03537
0.055	16.16997	0.175	14.00671
0.060	15.96729	0.180	13.98038
0.065	15.78112	0.185	13.95620
0.070	15.61013	0.190	13.93399
0.075	15.45308	0.195	13.91359
0.080	15.30884	0.200	13.89486
0.085	15.17635	0.205	13.87765
0.90	15.05466	0.210	13.86184
0.095	14.94289	0.215	13.84733
0.100	14.84024	0.220	13.83400
0.105	14.74595	0.225	13.82175
0.110	14.65935	0.230	13.81051
0.115	14.57981	0.235	13.80018
0.120	14.50676	0.240	13.79069
0.125	14.43966	0.245	13.78198

LITERATURE CITED

(1) Hsieh, J.S., Turian, R.M. and Tien, Chi, "Experimental Investigation of the Adsorption of Organic Contaminants in Waste Water on Granular Activated Carbon", FWPCA Research Report 69-1, November 1969.

(2) Crank, J., "The Mathematics of Diffusion", Oxford Press (1956).

(3) Weber, W.J., Jr. and Rumer, R.R., Jr., "Intraparticle Transport of Sulfonated Alkylbenzenes in a Porous Solid: Diffusion with Non-linear Adsorption", Water Resource Res., 1, 361 (1965).

(4) Digiano, F.A. and Weber, W.J., Jr., "Mathematical Modeling of Sorption Kinetics in Finite and Infinite-Bath Systems", Res. Rep. T-69-1, Dept. of Civil Engineering, Division of Sanitary and Water Resources Engineering, University of Michigan (1969).

(5) Tien, Chi and Thodos, George, "Ion Exchange Kinetics for Systems of Nonlinear Equilibrium Relationships", A.I.Ch.E.J. 5, 373 (1959).

(6) Tien, Chi, "Adsorption Kinetics of a Nonflow System with Nonlinear Equilibrium Relationship", A.I.Ch.E.J., 7, 410 (1961).

NOMENCLATURE

a = exponent of adsorption isotherm (Eq. II-1)

A = coefficient of adsorption isotherm (Eq. II-1)

b = radius of adsorbent

B = quantity defined by Eq. (II-18a)

C = liquid phase concentration

C^* = liquid phase concentration in equilibrium with solid phase concentration q^*

C_{B_E} = quantity appeared in the rate expression (Eq. II-2)

C_∞ = liquid phase concentration after infinite contact time

C_o = initial liquid phase concentration

C_b = bulk liquid phase concentration

C^+ = dimensionless concentration, defined by Eq. (II-23c)

D = internal diffusion coefficient

D_p = pore diffusion coefficient

F = quantity defined by Eq. (II-18b)

G = quantity defined by Eq. (II-18c)

k = chemical reaction rate constant [see Eq. (II-2)]

K_{j-k} = quantity defined by Eq. (II-16)

M = amount of adsorbent

q_i = point concentration in solid phase

q^* = solid phase concentration in equilibrium with liquid phase concentration C^*

q_∞ = concentration of adsorbent after infinite contact time

q = average solid phase concentration

q_s = solid phase concentration at the adsorbent surface

R = chemical reaction rate

r = radial distance

r^+ = dimensionless radial distance

S = concentration at the surface of the adsorbent matrix (pore diffusion model)

S^+ = dimensionless concentration, defined by Eq. (II-23d)

t^+ = dimensionless time, defined by Eq. (II-23b)

t = time

V = volume of liquid

Greek Letters

α = dimensionless concentration defined by Eq. (II-13a)

α_o = initial concentration parameter, defined as $(\frac{MA}{V})^{\frac{1}{a-1}} C_o$

β = dimensionless solid phase concentration defined by Eq. (II-13b)

δ = parameter defined by Eq. (II-13d)

ε = porosity of adsorbent

$\Delta\theta$ = dimensionless time increment

ϕ_1, ϕ_2 = constant defined by Eqs. (II-23e) and (II-23f)

APPENDIX I

Computer Program for Calculation of Concentration Histories for Internal Diffusion Model

```
C*************************************************************************
C
C     NUMERICAL SOLUTION OF SOLID DIFFUSION MODEL WITH CHANGING BLANK
C
C*************************************************************************
      IMPLICIT REAL * 8 (A-H,N-Z)
      DIMENSION A0(10),A(200),X(200),R(10,200),DT(200)
      FUNCA(P)=C*P**E+G*P**N+P-X0-G*XBE
      FUNCB(P)=C*P**E+G*P**N+P+F-G*XBE
      FUNCP(P)=C*E*P**(E-1.)+G*N*P**(N-1.)+1.
    1 READ(1,10) D1
   10 FORMAT(6F10.8)
    2 READ (1,300)  RA,DL,E,N,A0
  300 FORMAT(2F10.6,12F5.3)
      WRITE(3,50)  E,DL
   50 FORMAT('1FREUNDLICH EQUILIBRIUM EXPONENT=',F7.4,//' DELTA=',F8.4)
      DO 101 JJ=1,50
  101 DT(JJ)=D1
      DO 100   M=1,10
      C=(3.*DSQRT(DT(1))-(3./4.)*DT(1))/3.141592653589793
      D=3.*DSQRT(DT(1))/3.141592653589793
      G=DL*DT(1)
      X0=A0(M)
      XBE=X0*RA
      WRITE(3,200)M,X0,XBE
  200 FORMAT(' '//'*M=',I2,'INITIAL DIMENSIONLESS CONCENTRATION=',F6.4,/
     1,'     EQUILIBRIUM DIMENSIONLESS VALUE OF BLANK=',F6.4)
      X(1)=X0
      DO 7 I=1,20
      P=X(I)
      X(I+1)=X(I)-FUNCA(P)/FUNCP(P)
      ERR=.1D-4
      DEA=DABS(X(I+1)-X(I))
      IF(DEA-ERR) 11,11,7
    7 CONTINUE
      WRITE (3,21)
   21 FORMAT(' 19 ITERATIONS HAVE BEEN EXECUTED, A BETTER INITIAL GUESS
     1 IS NECESSARY ')
   11 X1=X(I+1)
      IF(X1-XBE) 27,27,28
   27 DL=0.0
   28 A(1)=X1
      DO 20 J=2,50
      C=(3.*DSQRT(DT(J))-(3./4.)*DT(J))/3.141592653589793
      D=3.*DSQRT(DT(J))/3.141592653589793
      G=DL*DT(J)
      J1=J-1
      XJ=J
      SUM=0.
      DO 30 K=1,J1
      XK=K
      U=2.*DSQRT(XJ-XK)-DSQRT(XJ-XK+1.)-DSQRT(XJ-XK-1.)
      SUM=SUM + U * (A(K)**E)
   30 CONTINUE
      F=-(SUM*D + A(J-1))
      X(1)=A(J-1)
      DO 14 L=1,20
      P=X(L)
      X(L+1)=X(L)-FUNCB(P)/FUNCP(P)
      DEB=DABS(X(L+1)-X(L))
```

```
      IF(DEB-ERR) 22,22,14
   14 CONTINUE
      WRITE (3,25)
   25 FORMAT(' 19 ITERATIONS HAVE BEEN EXECUTED, A BETTER INITIAL GUESS
     1 IS NECESSARY ')
   22 A(J)=X(L+1)
      IF(A(J)-XBE) 19,19,20
   19 DL=0.0
   20 CONTINUE
      DO 100 I=1,50
      R(M,I)=A(I)/A0(M)
  100 CONTINUE
      WRITE (3,55)
   55 FORMAT(' TIME',9X,'A0=0.44',4X,'A0=0.66',4X,'A0=1.03',4X,'A0=1.41'
     1,4X,'A0=1.68',4X,'A0=1.90',4X,'A0=2.25',4X,'A0=2.63',4X,'A0=2.96'
     2,4X,'A0=3.14')
      T=0.
      DO 65 I=1,50
      T=T+DT(I)
      WRITE(3,60) T,(R(M,I),M=1,10)
   60 FORMAT(' ',F10.8,2X,10(F9.5,2X))
   65 CONTINUE
      STOP
      END
```

APPENDIX II

Computer Program for Calculation of Concentration Histories
for Pore Diffusion Model

```
C*************************************************************************
C
C     NUMERICAL SOLUTION OF PORE DIFFUSION MODEL WITH CHANGING BLANK
C
C*************************************************************************
      IMPLICIT REAL * 8 (A-H,O-Z)
      DIMENSION C(50,11,2),DT(90),CS(11)
    1 READ(1, 9) D1
    9 FORMAT(7F10.8)
      READ(1,606)  N
  606 FORMAT(I5)
    2 READ (1,300)  AO,P2,RA,E,B
  300 FORMAT(5F10.6)
    3 READ (1,301) P1
  301 FORMAT (8F10.7)
      WRITE (3,302)  B,AO,P2
  302 FORMAT('1FREUNDLICH EQUILIBRIUM EXPONENT=',F7.4,//' AO=',F8.4,//
     1     ,' P2=',F8.4)
      DO 501 JJ=1,50
  501 DT(JJ)=D1
      CE=AO*RA
      ERR=.1D-3
      TT=0.
      M=N-1
      DO  4  L=1,M
      Q=L
      TT=TT+Q
    4 CONTINUE
      D=1./TT
      K=1
C
C        APPROXIMATE VALUE OF C(2,N-1,K)
C*************************************************************************
      Q=N
      H=N-2
      C(2,N-1,K)=((DT(1)/(2.*H*(D *(Q-H-1.))**2.))*(H+1.)*2.*AO)**(1./B)
      C(2,N-2,K)=((DT(1)/(2.*(H-1.)*(D *(Q-H))**2.))*H*1.*C(2,N-1,K))**
     1 (1./B)
      DO 22  L=1,3
C
C        TEST FOR BLANK CHANGING TERM
      IF(C(2,N-1,K)/2.-CE)   20,20,21
   20 Z=0.
      GO TO 22
   21 Z=(C(2,N-1,K)/2.-CE)**E
   22 C(2,N-1,K)=((DT(1)/(2.*H*(D *(Q-H-1.))**2.))*((H+1.)*2.*AO-2.*H*
     1 C(2,N-1,K)+(H-1.)*C(2,N-2,K))-C(2,N-1,K)-P2*Z*DT(1)/2.)**(1./B)
      CS(N-1)=C(2,N-1,K)
C
C        APPROXIMATE VALUES OF C(2,J,K),J=2,N-2
C     *****************************************************************
      M=N-2
      DO 200 J=2,M
      H=N-J-1
      LL=N-J
      DR=D*(Q-H-1.)
      C(2,LL,K)=((DT(1)/(2.*H*DR**2.))*(H+1.)*C(2,LL+1,K))**(1./B)
      CS(LL)=C(2,LL,K)
  200 CONTINUE
C
```

```
      APPROXIMATE VALUE OF C(2,1,K)
     ********************************************************************************
     DQ=D*(Q-1.)
     C(2,1,K)=(3.*DT(1)/DQ**2.)*(C(2,2,K)-C(2,2,K)*C(2,2,K)/C(2,3,K))-
    1 (C(2,2,K)*C(2,2,K)/C(2,3,K))**B
     CTANK=C(2,1,K)
     C(2,1,K)=DABS(CTANK)
     DO  202 L=1,3
     C(2,1,K)=(3.*DT(1)/DQ**2.)*(C(2,2,K)-C(2,1,K))-(C(2,1,K))**B
     CTANK=C(2,1,K)
     C(2,1,K)=DABS(CTANK)
202  CONTINUE
     CS(1)=C(2,1,K)

      APPROXIMATE VALUE OF C(2,N,K)
     ********************************************************************************
     F=0.
     F1=0.
     SUM=0.
     M=N-1
     DO 30 J=2,M
     S=J
     SUM=(D*(Q-S+1.))**3.*(C(2,J,K)+C(2,J,K)**B)*(S-1.)**2.
 30  F1=F1+SUM
     F=F1+(A0+A0**B)*(Q-1.)**2.*D**3.
     C(2,N,K)=A0-P2*DT(1)*((A0-CE)**E/2.+(A0-CE)**E/2.)-P1    *F

      VALUE OF C(2,N-1,K)
     ********************************************************************************
     H=N-2
     MM=1
250  CONTINUE
     MM=MM+1
     IF(MM-30)     257,258,258
258  GO TO  29
257  DO 28 L=1,2

      TEST FOR BLANK CHANGING TERM
     IF(C(2,N-1,K)/2.-CE)  25,25,26
 25  Z=0.
     GO TO 27
 26  Z=(C(2,N-1,K)/2.-CE)**E
 27  C(2,N-1,K)=((DT(1)/(2.*H*D **2.))*((H+1.)*(A0+C(2,N,K))-2.*H*
    1 C(2,N-1,K)+(H-1.)*C(2,N-2,K))-C(2,N-1,K)-P2*Z*DT(1)/2.)**(1./B)
     DIFF=C(2,N-1,K)-CS(N-1)
     IF(DABS(DIFF)-ERR*CS(N-1))  252,252,251
252  GO TO 28
251  CS(N-1)=C(2,N-1,K)
     GO TO 250
 28  CONTINUE
 29  CONTINUE

      VALUE OF C(2,J,K),J=2,N-2
     ********************************************************************************
     M=N-2
     DO   950 J=2,M
     H=J-1
     DR=D*(Q-H-1.)
     MM=1
772  CONTINUE
```

```
      MM=MM+1
      IF(MM-30)        720,721,721
  721 GO TO  950
  720 DO 960 L=1,2

          TEST FOR BLANK CHANGING TERM
      IF (C(2,J,K)/2.-CE)  970,970,971
  970 Z=0.
      GO TO 972
  971 Z=(C(2,J,K)/2.-CE)**E
  972 CC=(C(2,J,K))**B
      IF (CC-C(2,J,K))     511,511,512
  511 CTANK=((DT(1)/(2.*H*DR**2.))*((H+1.)*C(2,J+1,K)-2.*H*C(2,J,K)+(H-1
     1 .)*C(2,J-1,K))-(C(2,J,K))**B)-P2*Z*DT(1)/2.
      C(2,J,K)=DABS(CTANK)
      DIFF=C(2,J,K)-CS(J)
      IF(DABS(DIFF)-ERR*CS(J))      770,770,771
  770 GO TO 960
  771 CS(J)=C(2,J,K)
      GO TO 772
  512 CTANK=((DT(1)/(2.*H*DR**2.))*((H+1.)*C(2,J+1,K)-2.*H*C(2,J,K)+(H-1
     1.)*C(2,J-1,K))-C(2,J,K))-P2*Z*DT(1)/2.
      CTANK=DABS(CTANK)
      C(2,J,K)=(CTANK)**(1./B)
      DIFF=C(2,J,K)-CS(J)
      IF(DABS(DIFF)-ERR*CS(J))    773,773,774
  773 GO TO 960
  774 CS(J)=C(2,J,K)
      GO TO 772
  960 CONTINUE
  950 CONTINUE

          VALUE OF C(2,1,K)
      ********************************************************************************
      DQ=D*(Q-1.)
      MM=1
  775 CONTINUE
      MM=MM+1
      IF(MM-30)          724,725,725
  725 GO TO 981
  724 DO 980 L=1,2
      CTANK    =(3.*DT(1)/DQ**2.)*(C(2,2,K)-C(2,1,K))-(C(2,1,K))**B
      C(2,1,K)=DABS(CTANK)
      DIFF=C(2,1,K)-CS(1)
      IF(DABS(DIFF)-ERR*CS(1)) 776,776,777
  776 GO TO 980
  777 CS(1)=C(2,1,K)
      GO TO 775
  980 CONTINUE
  981 CONTINUE

C         VALUE OF C(2,N,K)

C     ********************************************************************************
      DO 60 L=1,3
      F=0.
      SUM=0.
      DO 55 J=2,N
      S=J
      SUM=(D*(Q-S+1.))**3.*(C(2,J,K)+C(2,J,K)**B)*(S-1.)**2.
```

```
      F=F+SUM
   55 CONTINUE
      IF(C(2,N,K)-CE)   710,710,711
  710 Z=0.
      GO TO 712
  711 Z=(C(2,N,K)-CE)**E
  712 C(2,N,K)=A0-P2*DT(1)*((A0-CE)**E/2.+Z)-P1    *F
   60 CONTINUE

      DO 900 I=2, 49

         APPROXIMATE VALUE OF C(I+1,1,K)
         TEST FOR BLANK CHANGING TERM
      ********************************************************************************
      IF(C(I,1,K)-CE) 70,70,71
   70 Z=0.
      GO TO 75
   71 Z =(C(I,1,K)-CE)**E
   75 CC=(C(I,1,K))**B
      IF(CC-  C(I,1,K))   700,700,701
  700 CTANK=C(I,1,K) -P2*Z*DT(I)/2.+(3.*DT(I)/DQ**2.)*2.*C(I,2,K)
      C(I+1,1,K)=DABS(CTANK)
      GO TO 702
  701 CTANK     =(C(I,1,K)**B-P2*Z*DT(I)/2.+(3.*DT(I)/DQ**2.)*2.*
     1 C(I,2,K))
      CTANK=DABS(CTANK)
      C(I+1,1,K)=(CTANK)**(1./B)
  702 CONTINUE

         APPROXIMATE VALUES OF(C(I+1,J,K)J=2,N-1)
      ********************************************************************************
      M=N-1
      DO 80 J=2,M
      G=J-1
      DR=D*(Q-G-1.)

         TEST FOR BLANK CHANGING TERM
      IF(C(I,J,K)-CE) 72,72,73
   72 Z=0.
      GO TO 74
   73 Z=(C(I,J,K)-CE)**E
   74 CC=(C(I,J,K))**B
      IF (CC-  C(I,J,K))   750,750,751
  750 CTANK=C(I,J,K)+(DT(I)/(2.*G*DR**2.))*((G+1.)*2.*C(I,J+1,K)-
     1 2.*G*2.*C(I,J,K)+(G-1.)*2.*C(I,J-1,K))-P2*Z*DT(I)/2.
      C(I+1,J,K)=DABS(CTANK)
      GO TO 752
  751 CTANK     =(C(I,J,K)**B+(DT(I)/(2.*G*DR**2.))*((   G+1.)*2.
     1 *C(I,J+1,K)-2.*G*2.*C(I,J,K)+(  G-1.)*2.*C(I,J-1,K))-P2*Z
     2                  *DT(I)/2.)
      CTANK=DABS(CTANK)
      C(I+1,J,K)=(CTANK)**(1./B)
  752 CONTINUE
   80 CONTINUE

         APPROXIMATE VALUE OF C(I+1,N,K)
      ********************************************************************************
      SUM=0.
      FF1=0.
      FF=0.
```

```
      TEST FOR BLANK CHANGING TERM
    M=I
    DO 90 II=2,M
    IF(C(II,N,K)-CE) 81,81,82
 81 Z=0.
    GO TO 83
 82 Z=    (C(II,N,K)-CE)**E
 83 SUM=Z
 90 FF1=FF1+SUM

      TEST FOR BLANK CHANGING TERM
    IF(C(I,N,K)-CE)  84,84,85
 84 Z=0.
    GO TO 86
 85 Z=(C(I,N,K)-CE)**E/2.
 86 FF=FF1+(  AO    -CE)**E/2.+Z
    F=0.
    F1=0.
    SUM=0.
    M=N-1
    DO 87 J=2,M
    S=J
    SUM=(D*(Q-S+1.))**3.*(C(I+1,J,K)+C(I+1,J,K)**B)*(S-1.)**2.
 87 F1=F1+SUM
    F=F1+(C(I,N,K)+C(I,N,K)**B)*(Q-1.)**2.*D**3.
    C(I+1,N,K)=AO-P2*DT(I)*FF-P1   *F

      VALUE OF  C(I+1,1,K)
    ************************************************************************
    MM=1
780 CONTINUE
    MM=MM+1
    IF(MM-30)       730,731,731
731 GO TO 119
730 DO 100  L=1,2

      TEST FOR BLANK CHANGING TERM
    IF((C(I+1,1,K)+C(I,1,K))/2.-CE)  101,101,102
101 Z=0.
    GO TO 103
102 Z=((C(I+1,1,K)+C(I,1,K))/2.-CE)**E
103 CC=(C(I+1,1,K))**B
    IF(CC-C(I+1,1,K))  104,104,105
104 C(I+1,1,K)= C(I,1,K)-(C(I+1,1,K)**B-C(I,1,K)**B)-P2*Z
   1                      *DT(I)/2.+(3.*DT(I)/DQ**2.)*((C(I+1,2,K)+
   2 C(I,2,K))-(C(I+1,1,K)+C(I,1,K)))
    CTANK=C(I+1,1,K)
    C(I+1,1,K)=DABS(CTANK)
    DIFF=C(I+1,1,K)-CS(1)
    IF (DABS(DIFF)-ERR*CS(1))       781,781,782
781 GO TO 100
782 CS(1)=C(I+1,1,K)
    GO TO 780
105 CTANK     =(C(I,1,K)**B-(C(I+1,1,K)-C(I,1,K))-P2*Z
   1                      *DT(I)/2.+(3.*DT(I)/DQ**2.)*((C(I+1,2,K)+
   2 C(I,2,K))-(C(I+1,1,K)+C(I,1,K))))
    CTANK=DABS(CTANK)
    C(I+1,1,K)=(CTANK)**(1./B)
    DIFF=C(I+1,1,K)-CS(1)
```

```
      IF (DABS(DIFF)-ERR*CS(1))  783,783,784
783   GO TO 100
784   CS(1)=C(I+1,1,K)
      GO TO 780
100   CONTINUE
119   CONTINUE

         VALUES OF(C(I+1,J,K)J=2,N-1)
      ********************************************************************************
      M=N-1
      DO 115 J=2,M
      G=J-1
      DR=D*(Q-G-1.)
      MM=1
790   CONTINUE
      MM=MM+1
      IF(MM-30)      734,735,735
735   GO TO 115
734   DO 110 L=1,2

         TEST FOR BLANK CHANGING TERM
      IF((C(I+1,J,K)+C(I,J,K))/2.-CE)  111,111,112
111   Z=0.
      GO TO 113
112   Z= ((C(I+1,J,K)+C(I,J,K))/2.-CE)**E
113   CC=(C(I+1,J,K))**B
      IF (CC-C(I+1,J,K))     114,114,116
114   CTANK      = C(I,J,K)    +(DT(I)/(2.*G*DR**2.))*((  G+1.)*(C(I,J+1,K
     1)+C(I+1,J+1,K))-2.*G*(C(I,J,K)+C(I+1,J,K))+(  G-1.)*(C(I,J-1,K)+
     2C(I+1,J-1,K)))-(C(I+1,J,K)**B-C(I,J,K)**B)-P2*Z*DT(I)/2.
      C(I+1,J,K)=DABS(CTANK)
      DIFF=C(I+1,J,K)-CS(J)
      IF(DABS(DIFF)-ERR*CS(J))        791,791,792
791   GO TO 110
792   CS(J)=C(I+1,J,K)
      GO TO 790
116   CTANK      =(C(I,J,K)**B+(DT(I)/(2.*G*DR**2.))*((  G+1.)*(C(I,J+1,K
     1 )+C(I+1,J+1,K))-2.*G*(C(I,J,K)+C(I+1,J,K))+(G-1.)*(C(I,J-1,K)+
     2C(I+1,J-1,K)))-(C(I+1,J,K)-C(I,J,K))-P2*Z
     3            *DT(I)/2.)
      CTANK=DABS(CTANK)
      C(I+1,J,K)=(CTANK)**(1./B)
      DIFF=C(I+1,J,K)-CS(J)
      IF(DABS(DIFF)-ERR*CS(J))     793,793,794
793   GO TO 110
794   CS(J)=C(I+1,J,K)
      GO TO 790
110   CONTINUE
115   CONTINUE

         VALUE OF C(I+1,N,K)
      ********************************************************************************
      DO 899 L=1,3
      SUM=0.
      FF1=0.
      FF=0.
      M=I
      DO 130 II=2,M

         TEST FOR BLANK CHANGING TERM
```

```
    IF(C(II,N,K)-CE)  121,121,122
121 Z=0.
    GO TO 123
122 Z=(C(II,N,K)-CE)**E
123 SUM=Z
130 FF1=FF1+SUM

       TEST FOR BLANK CHANGING TERM
    IF(C(I+1,N,K)-CE)124,124,125
124 Z=0.
    GO TO 126
125 Z=(C(I+1,N,K)-CE)**E/2.
126 FF=FF1+(   A0    -CE)**E/2.+Z
    F1=0.
    SUM=0.
    DO 140 J=2,N
    S=J
    SUM=(D*(Q-S+1.))**3.*(C(I+1,J,K)+C(I+1,J,K)**B)*(S-1.)**2.
140 F1=F1+SUM
    C(I+1,N,K)=A0-P2*DT(I)*FF-P1    *F1
899 CONTINUE
900 CONTINUE
    WRITE (3,405)
405 FORMAT('1',' TIME',9X,'P1=2.304E-4')
    T=0.
    DO 605 I=1,49
    T=T+DT(I)
    WRITE(3,600)  T, C(I+1,N,1)
600 FORMAT(' ',F10.8,2X,10(F9.5,2X))
605 CONTINUE
    STOP
    END
```